Hydrated aluminum powder for direct alloying of steel and alloys - challenges of the future

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Abstract
The presented study considers and substantiates the possibility of increasing the efficiency of the technology of out-of-furnace, direct alloying of steel and alloys, through the combined use of hydrogen - and aluminothermic methods of reducing target metals from metal-oxide ore or technogenic powdered materials. To achieve this goal, it is proposed to use hydrogenated aluminum powder (1–5% AlH₃), obtained as a result of hydro-vacuum dispersion of molten secondary aluminum, as a reducing agent. The morphology of the obtained powder particles containing different allotropic modifications of aluminum hydride is shown. Chemical features and advantages of the proposed process are discussed. The practical value and perspectivity of the development of this approach are argued.

Keywords:
steel alloying
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Current state of the problem

The task of reducing the specific consumption of expensive ferroalloys and ligatures in need of scarce ores is acute for modern electrometallurgy of steel and alloys [1, 2]. The noted problem, in the future, will gradually become even more aggravated due to the long-term strategy of achieving climate neutrality of the world economy [3], tightening quotas and raising taxes on greenhouse carbon dioxide emissions [4, 5], increasing energy prices [6], reducing metallurgical value, conditionality and number of mined ore [7, 8], the need to increase the degree of compensation for this shortage with re-processed technogenic resources [9, 10], etc. The aggravation of the problem of seeking rational ways of ecological and economical safely of the ferroalloy industry [11, 12] will undoubtedly entail the steel and alloy industry. Therefore, the issue of replacing traditional ferroalloys with other, cheaper, but metallurgically effective materials is becoming increasingly relevant. Great potential for solving this problem lies in the development of technology for direct alloying of steel and alloys, which provides for the direct reduction of target alloying components (manganese, chromium, nickel, titanium, silicon, calcium, boron, etc.) from oxide materials fed into the ladle furnace together with reducing agents, in briquetted or granulated form [13-16].

The process of direct alloying is effective in a wide range of the amount of additive metal-oxide ore, which allows to alloy carbon and low-alloyed steels with the coefficient of useful use (recovery) of leading elements not less than 0.95–0.97 [14, 15]. The main factor limiting the application of direct alloying technology in the conditions of out-of-furnace processing, steel and alloys, is the increase in the amount of slag in the ladle [16]. Consequently, there is a necessity to perform an additional operation of slag downloading from the ladle, which slightly complicates the implementation of the technology, but by putting into operation the innovative installation of hydro-vacuum vertical suction and slag granulation [17], developed by us, this problem can be solved with minimum energy costs and operating time.
According to the noted study [16] higher performance can be achieved by applying direct alloying technology under oxidizing conditions in order to increase the residual manganese content in the metal before out-of-furnace treatment. This study uses the example of direct manganese alloying to show that the determining factor in the efficiency of this process is the current carbon content of the steel, which acts as a reducing agent for manganese from its oxides. It is shown that by the technology of direct alloying, at melting of medium- and high-carbon steels, the manganese content in the melt can be increased to 0.6 % and more. This approach is certainly progressive, but its implementation is possible only in the presence of excess carbon in the alloyed melt. For low-carbon or special high-alloy steels and alloys [18], the method of aluminothermic reduction of target metals, from oxide ores or technogenic formations [19, 20] remains a more acceptable universal approach. But, in the future, with the development of more environmentally friendly and technoeconomically efficient technologies of hydrogen reduction of metals, the method of aluminum heat treatment may still lose its leadership [21, 22]. However, at this stage of development, direct application of gas hydrogen in the technology of direct alloying of steel and alloys is impossible due to its ultrafast volatility. And manufacturing of special hydrogen-holding sealed high-pressure reaction chambers, is associated with significant costs and technical difficulties of maintenance, so this approach is not yet practiced at all in the modern industry of manganese and manganese-based alloys.

Presently, the problem of hydrogen reduction of metal-oxide materials can be successfully solved by its sequential combination with the aluminothermic reduction process. A successful example of such a solution is the study [23] and its proposed process-HalMan. The results obtained on the example of hydrogen-alumothermal reduction of manganese oxides to produce alumo-manganese and ferromanganese alloys are the most encouraging and ecologically effective, but its direct use in the processes of direct alloying of steel and alloys is also impossible due to the need for a special hydrogen reaction chamber.
The sequence of reductive reactions occurring in the noted two-step HalMan-process [23] with indication of the molar enthalpy of occurrence of these reactions is as follows:

\[ 2\text{MnO}_2 + \text{H}_2^{(\text{Gas})} = \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}^{(\text{Gas})} \]
\[ \Delta H^\circ (298K) = -163,7 \text{ кДж/моль} \] (1)

\[ 3\text{Mn}_2\text{O}_3 + \text{H}_2^{(\text{Gas})} = 2\text{Mn}_3\text{O}_4 + \text{H}_2\text{O}^{(\text{Gas})} \]
\[ \Delta H^\circ (298K) = -135,1 \text{ кДж/моль} \] (2)

\[ \text{Mn}_3\text{O}_4 + \text{H}_2^{(\text{Gas})} = 3\text{MnO} + \text{H}_2\text{O}^{(\text{Gas})} \]
\[ \Delta H^\circ (298K) = -16,6 \text{ кДж/моль} \] (3)

\[ 3\text{MnO} + 2\text{Al}^{(\text{Sol})} = 3\text{Mn} + \text{Al}_2\text{O}_3^{(\text{Liq})} \]
\[ \Delta H^\circ (298K) = -520 \text{ кДж/моль} \] (4)

From the above sequence (1-3) it can be seen that manganese in the ore part of the granulated charge is reduced by hydrogen to the divalent state MnO (Mn''"), after which it is fed to the furnace with aluminum reducing agent and reduced to metallic manganese (4). Due to the fact that reactions (1-3) are weakly exogenous, according to Le Chatelier's principle [24], it is necessary to increase the temperature and remove water vapor from the reaction zone. Since the process needs external energy stimulation (heating up to 500-1000K), the heat released at the stage of aluminothermic reduction of manganese in a three-electrode batch electric melting furnace is used for this purpose [23]. According to the results of the noted research, on average, under the condition of heat recovery by 40%, the reduction of specific consumption of electrical energy per kilogram of the produced product can reach 22-128 kWh, depending on the degree of oxidation and coarseness of the reduced ore raw material.

**Perspectives for development**

Based on the above analysis, we concluded that there is a new possibility of improving the technology of direct alloying of steel and alloys, which is associated with the prospect of using as an active reducing agent obtained specifically for this purpose hydrogenated aluminum powder AlH$_3$ (H 1-5%). We were the first to obtain such a powder as a by-product of hydro-vacuum dispersion of liquid aluminum
superheated at 150 °C. The observed effect was achieved by operating our hydro-vacuum dispersion unit [25] in the mode of generating a high-frequency cavitation-wave field [26] and initiating sonochemical hydrogenation reactions. According to the study of [27], the general sonochemical hydrogenation reaction of metal powder particles can be written as follows:

\[
\text{Me} + \frac{x}{2}\text{H}_2 \rightarrow \text{MeH}_x
\]  (5)

The results of sonochemical hydrogenation of powdered aluminum particles produced in our hydro-vacuum melt dispersion unit are illustrated in Figure 1.

![Figure 1](image)

**Figure 1**
Aluminum hydride inclusions of \(\alpha\) (a) and \(\alpha'\) (b) allotropic modifications in powdered aluminum particles obtained by hydro-vacuum dispersion method
Figure 1(a) shows that a suspension mixture of ordinary aluminum with prism-shaped inclusions of particles of aluminum hydride $\text{AlH}_3 \alpha$ allotropic modification was obtained. In turn, figure 1(b) illustrates the effect of its transformation into the more unstable $\alpha'$ allotropic modification, which is the result of 6 days dehydration drying of the marked powder particles in air (20-25 °C). More unstable $\gamma$ and $\beta$ modifications (Fig. 2) of aluminum hydride $\text{AlH}_3$ were also found in small amounts, identically to the results presented in the study [28].
Preliminary experimental work to evaluate the effectiveness of powder aluminum with aluminum hydride inclusions for the technology of direct alloying of steel and alloys has shown very positive and encouraging results. In particular, it was found that the joint (simultaneous) reaction of aluminum and hydrogen retained in its crystal lattices with oxides of target metals can lead to an increase in the extraction coefficient of these metals while reducing the time required for this. The main factor of such progress is the increase in the degree of useful use of hydrogen, which was achieved by reducing its consumption (losses) for volatilization with water vapor released in the process. This was provided as a result of forced compaction of direct alloying briquettes by applying pressing pressure with a power of 10 MPa.

Physical modelling of the process of direct alloying of steel and alloys in laboratory conditions has shown that hydrogen bound to aluminum, being in dense contact with reduced complex oxide components, being in briquettes for direct alloying of steel, at getting in a surface slag layer of mini ladle-furnace (volume 0.003 m$^3$) and heating up to 130-200 °C, started outrunning emission, reaction and reduction of target metals to simple monoxides (identical to reactions 1-3). The reaction water vapor released in this process, getting into the slag layer of the mini ladle-furnace, performed the function of a loosening agent generated from the bubbling effect. Excited wave action and accompanying convection hydrodynamic flows promoted intensive mixing of pure metal droplets, recovered after the subsequent exothermic reaction with aluminum particles, in the main volume of alloyed steel.

The summary reaction of complex alumino-hydrogen reduction of a metal (in this case - manganese) from its dioxide, can be written as follows:

$$3\text{MnO}_2 + 2\text{AlH}_3 = 3\text{Mn}↓ + \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \uparrow \Delta\text{H}^\circ(298\text{K})=-834,4 \text{ кДж/моль} \quad (6)$$

A systematic analysis of the results of experimental studies, which were carried out using manganese concentrate
with a manganese content of 48-51%, showed that due to the intensification of reducing processes in the briquettes of direct alloying of steel and alloys, the specific consumption of aluminum, depending on the degree of its hydrogenation (1-5%) and particle size distribution (200-1000 μm), on average decreased by 3-5%, manganese recovery coefficient reached 0.97-0.99, duration of the chemical-physical process of reduction and dissolution of alloying manganese in the alloyed steel was reduced by 10-15%, and degree of its uniform distribution increased to 90-95%. It was recorded that the higher the amount of manganese required for alloying steel, and therefore, more direct alloying briquettes with hydrogenated aluminum are added in liquid metal, the higher the overall (techno-economic-ecological) efficiency of the alloying process.

It should be emphasized that the use of hydrogenated aluminum powder obtained by us is not associated with increased costs for the production of direct alloying briquettes, as the implementation of the technology of hydro-vacuum dispersion and hydrogenation of melts makes it possible to use comparatively cheap secondary aluminum as a metal-containing raw material, since the proposed process itself provides melt purification from harmful non-metallic impurities and inclusions, i.e. there is no strict need to use chemically pure aluminum. This significantly reduces the cost of production of powder and direct alloying briquettes produced from it. Powders produced by the hydro-vacuum method are 20-30% cheaper compared to analogues, since in this case there is no need to use expensive inert gases that prevent oxidation of the powder particles produced. The specific maintenance costs of the hydro-vacuum dispersing unit are not high, as its productivity is almost 10 times higher than traditional methods of water-jet, gas or centrifugal atomization. The unit operates reliably and safely, without emission of environmentally harmful substances. The plant can be easily installed in practically any aluminum casting workshop, without downtime and substantial reconstruction of the latter.

**Conclusion**

Based on the above it can be concluded that:
Hydro-vacuum production and metallothermic application of hydrogenated aluminum powder for the production of briquettes for direct alloying of steel and alloys, is effective and promising, both from the point of view of improving the technology of direct alloying of steel and alloys itself, and - reducing the specific consumption of this powder reducing agent;

- the proposed approach will provide both reduction of the cost of direct alloying process and improve the overall energy and environmental benefits of high-tech recycling of relatively cheap secondary aluminum;

- By mastering the technological peculiarities of hydrogenation of the powder obtained by hydro-vacuum dispersion of liquid secondary aluminum, it will be possible to use it as an active reducing agent in the technological scheme of HalMan-process [23, 29], which in the future may further increase the efficiency of this project under development.

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